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Catalytic Hydrothermal Liquefaction of Mango Waste over Template-Synthesized $NiFe_2O_4$/Biochar Catalyst

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Abstract

Hydrothermal liquefaction (HTL) offers a promising pathway for converting wet organic waste into liquid fuels; however, the high oxygen content of bio-crude derived from fruit waste remains a major limitation. This study aims to valorize mango fruit waste (MFW) into upgraded bio-crude oil through catalytic HTL using a template-synthesized activated biochar-supported $NiFe_2O_4$ bimetallic catalyst. The feedstock and catalyst were characterized using proximate and ultimate analyses, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and gas chromatography–mass spectrometry (GC–MS). Mango fruit waste showed favorable hydrothermal conversion characteristics, including high volatile matter content, a carbon content of 48.07 wt%, and a higher heating value (HHV) of 14.32 MJ kg^{-1}. The incorporation of the $NiFe_2O_4$-activated biochar catalyst substantially improved bio-crude quality compared with non-catalytic HTL, increasing the carbon content to 63.53 wt% and the HHV to 16.66 MJ kg^{-1}. GC–MS analysis revealed a marked compositional shift toward aromatic hydrocarbons, phenolic compounds, and nitrogen-containing heterocycles, indicating enhanced deoxygenation, hydrogen transfer, and aromatization reactions promoted by the bimetallic catalyst. The study concludes that template-engineered biochar-supported $NiFe_2O_4$ catalysts are effective for upgrading oxygen-rich intermediates during fruit waste HTL. These findings contribute to sustainable waste valorization and biofuel production by demonstrating the potential of mango fruit waste as a viable feedstock for producing improved bio-crude oil.

Keywords: Activated Biochar; Bio-Crude Oil; Hydrothermal Liquefaction; Mango Fruit Waste; $NiFe_2O_4$ Catalyst

INTRODUCTION

The growing global demand for energy, coupled with concerns over climate change and environmental pollution, has intensified interest in sustainable energy conversion technologies using renewable and waste-derived resources. Biomass-based fuels are particularly attractive due to their carbon-neutral potential and ability to reduce fossil fuel dependence (Peterson *et al.*, 2008; Zhou *et al.*, 2023). Food and fruit wastes represent a rapidly increasing fraction of municipal solid waste, especially in developing countries, where poor waste management contributes to greenhouse gas emissions, water contamination, and public health challenges (Singh *et al.*, 2022).

Hydrothermal liquefaction (HTL) has emerged as a promising thermochemical pathway for converting wet biomass directly into energy-dense bio-crude oil without energy-intensive drying (Akhtar *et al.*, 2019; Toor *et al.*, 2022). Operating under subcritical water conditions (250–370°C, 10–35 MPa), HTL facilitates hydrolysis, depolymerization, and recombination to yield bio-crude with lower oxygen content and higher heating value than fast pyrolysis products (Gollakota *et al.*, 2018; Xu et al., 2020). Catalytic HTL further enhances yield and quality via deoxygenation, decarboxylation, denitrogenation, and aromatization (Huang *et al.*, 2021; Wang *et al.*, 2023). While homogeneous catalysts like alkali salts accelerate kinetics, they pose recovery, corrosion, and contamination issues (Akhtar *et al.*, 2019). Heterogeneous catalysts, particularly activated biochar-supported metal and bimetallic systems, offer recyclability, selectivity, and stability due to high surface area and tunable functionality (Cheng *et al.*, 2016; Kozhukhova & Titirici, 2023; Leng *et al.*, 2020).

Nickel- and iron-based catalysts excel in hydrogen transfer, C–O bond cleavage, and aromatic stabilization under hydrothermal conditions (Huang *et al*., 2021).

Despite these advances, template-synthesized activated biochar-supported bimetallic catalysts, such as $NiFe_2O_4$, remain largely unexplored for HTL of fruit wastes like mango fruit waste (MFW). Mango processing generates carbohydrate- and oxygen-rich peel and pulp residues, necessitating targeted upgrading for fuel-grade bio-crude, yet no systematic studies exist on $NiFe_2O_4$/biochar systems for this feedstock (Li *et al*., 2018; Singh *et al*., 2022).

This study investigates catalytic HTL of MFW using template-synthesized activated biochar-supported $NiFe_2O_4$, emphasizing feedstock suitability, catalyst structure–function relationships, and bio-crude quality improvements. The work advances sustainable waste-to-energy technologies within circular bioeconomy principles.

MATERIALS AND METHODS

Materials

Mango fruit waste (MFW) was collected from local processing facilities in Bauchi, Nigeria. Analytical-grade nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), and chemical activants (KOH) were procured from Sigma-Aldrich. Deionized water and dichloromethane (DCM) were used as solvents. The biomass precursor for activated biochar was rice husk.

Feedstock Preparation

MFW was thoroughly washed with deionized water to remove dirt and impurities, oven-dried at 105°C for 24 h, milled using a hammer mill, and sieved to <1 mm particle size for uniform processing.

Catalyst Synthesis

Activated biochar (AC) was prepared via template-assisted pyrolysis of rice husk at 800°C under N_2 flow, followed by KOH chemical activation (1:3 ratio) at 900°C. $NiFe_2O_4$ precursors were impregnated onto AC by wet impregnation (Ni:Fe molar ratio 1:2, 10 wt% total metal loading), dried at 110°C, and calcined at 500°C for 4 h under air to form $NiFe_2O_4$/AC catalyst.

Characterization Methods

Feedstock characterization: Proximate analysis (moisture, volatiles, ash, fixed carbon) followed ASTM E870; ultimate analysis (C, H, N, S, O by difference) used CHNS elemental analyzer (model vario EL cube); HHV was determined by bomb calorimetry (IKA C200) as shown in Tables 1 and 2. Functional groups were identified via Fourier Transform Infrared (FTIR) spectroscopy (Figure 1), and thermal behavior via Thermogravimetric Analysis (TGA) at 10°C/min under N_2 (Figure 2).

Catalyst characterization: Morphology was examined by Scanning Electron Microscopy (SEM); crystallinity by X-ray Diffraction (XRD, Figure 3); textural properties (BET surface area, pore volume, pore size) by N_2 physisorption (Table 3, Figure 4); surface functional groups by FTIR (Figure 5).

Hydrothermal Liquefaction Procedure

HTL experiments were conducted in a 500 mL stainless steel batch reactor (Parr 4560). MFW (20 g) was loaded with deionized water (biomass:water ratio 1:8) ± catalyst (5 wt%). The reactor was purged with N_2, heated to 320°C (10°C/min), held for 30 min (final pressure ~18 MPa), then rapidly cooled in an ice bath. Products were separated: bio-crude via DCM extraction (3×50 mL), aqueous phase by centrifugation, solids by filtration. Yields were calculated gravimetrically on dry ash-free basis.

Product Analysis Methods

Bio-crude elemental composition and HHV followed the same methods as feedstock (Table 4). Molecular composition was determined by Gas Chromatography-Mass Spectrometry (GC-MS, Agilent 7890B) (Figure 7). Temperature effects on yields were assessed (Figure 6).

RESULTS AND DISCUSSION

Feedstock Properties

Mango fruit waste exhibited physicochemical properties favourable for hydrothermal processing, including high volatile matter content, moderate ash levels, and an HHV of 14.32 MJ kg^{-1}. These characteristics are comparable to those reported for other fruit and food wastes processed via HTL (Li et al., 2018; Singh et al., 2022). However, the relatively high oxygen content (42.44 wt%) suggests that non-catalytic HTL would yield oxygen-rich bio-crude, underscoring the need for catalytic upgrading (Gollakota *et al.,* 2018). As shown in Tables 1 and 2, MFW exhibited high volatile matter (61.24 wt%) and oxygen content (42.44 wt%), with HHV of 14.34 MJ/kg, favorable for HTL (Figure 1 FTIR; Figure 2 TGA)

Table 1: Ultimate Analysis of Mango Fruit Waste

Ultimate analysis	
Element	**(Wt.%)**
Carbon (C)	48.065
Hydrogen (H)	6.692
Nitrogen (N)	2.786
Sulfur (S)	0.014
Oxygen (O)	42.443
Higher Heating Value (HHV) MJ/kg	14.342

Table 2: Proximate Analysis of Mango Waste Fruit

Proximate analysis	
Parameter	**Wt. %**
Moisture Content (%)	12.179
Volatile Matter (%)	61.240
Ash Content (%)	6.687
Fixed Carbon (%)	19.894
Total	100
Crude Fiber (%)	18.000
Crude Fat (%)	9.200
Crude Protein (%)	7.500
Total Carbohydrates (%)	46.000

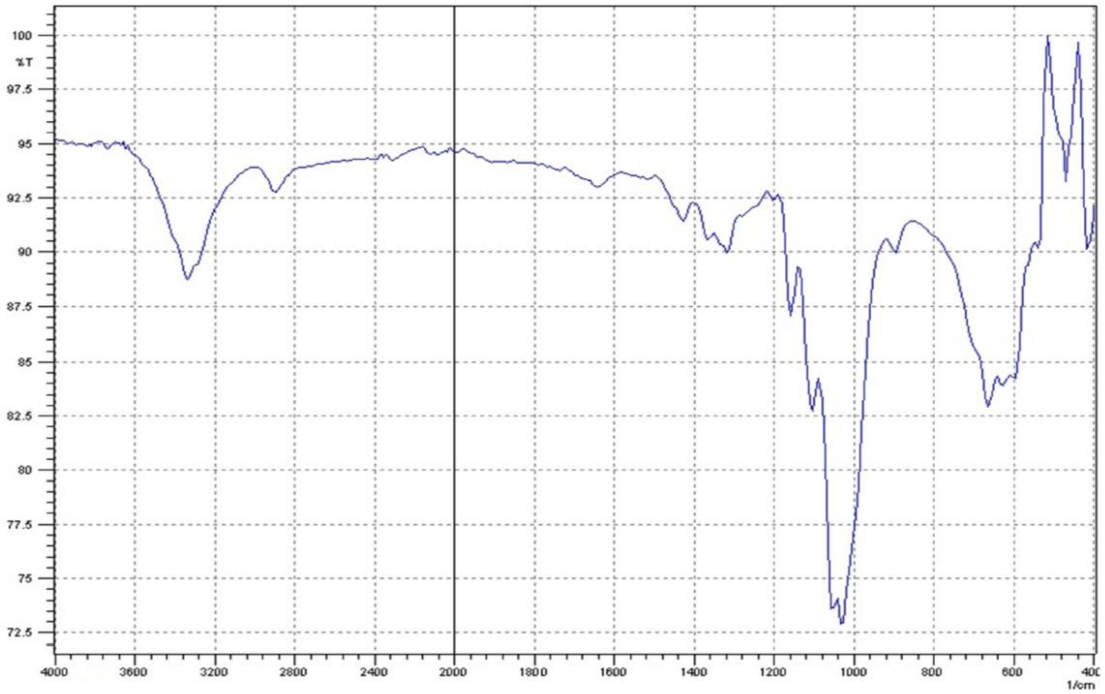

Figure 1: FTIR spectra Mango Fruit Waste

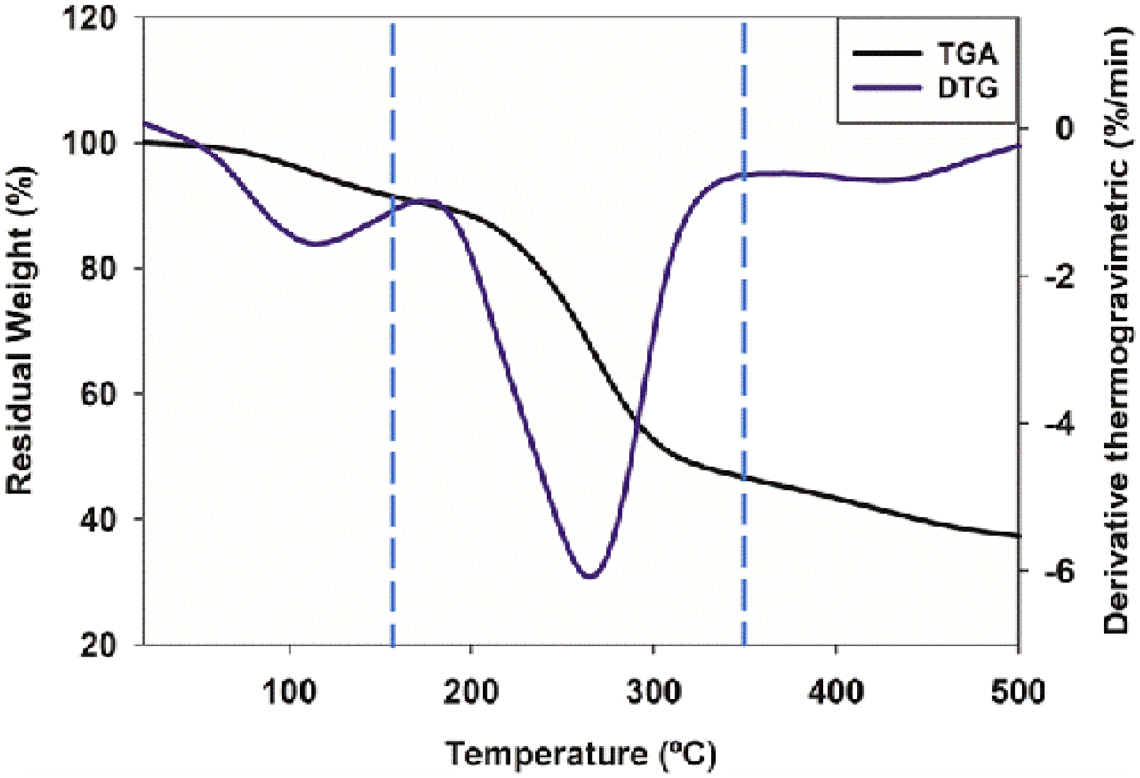

Figure 2: Thermogravimetric and Derivate thermogravimetric Analysis for MFW at a Heating Rate of 10°C/min

Catalyst Characteristics

BET analysis confirmed that the template-synthesized activated biochar possessed a high surface area and well-developed pore network, enabling effective dispersion of the $NiFe_2O_4$ phase. XRD patterns verified the formation of crystalline spinel $NiFe_2O_4$, while SEM images revealed uniform distribution of catalyst particles across the biochar surface. These structural features are critical for enhancing mass transfer and catalytic accessibility during hydrothermal reactions (Kozhukhova & Titirici, 2023). Table 3 and Figure 4 confirm high AC surface area (1097.96 m^2/g) reduced to 543.17 m^2/g post-$NiFe_2O_4$ loading, maintaining mesoporosity. XRD (Figure 3) verified spinel $NiFe_2O_4$ phase; SEM and FTIR (Figure 5) showed uniform dispersion and functional groups enhancing hydrothermal stability.

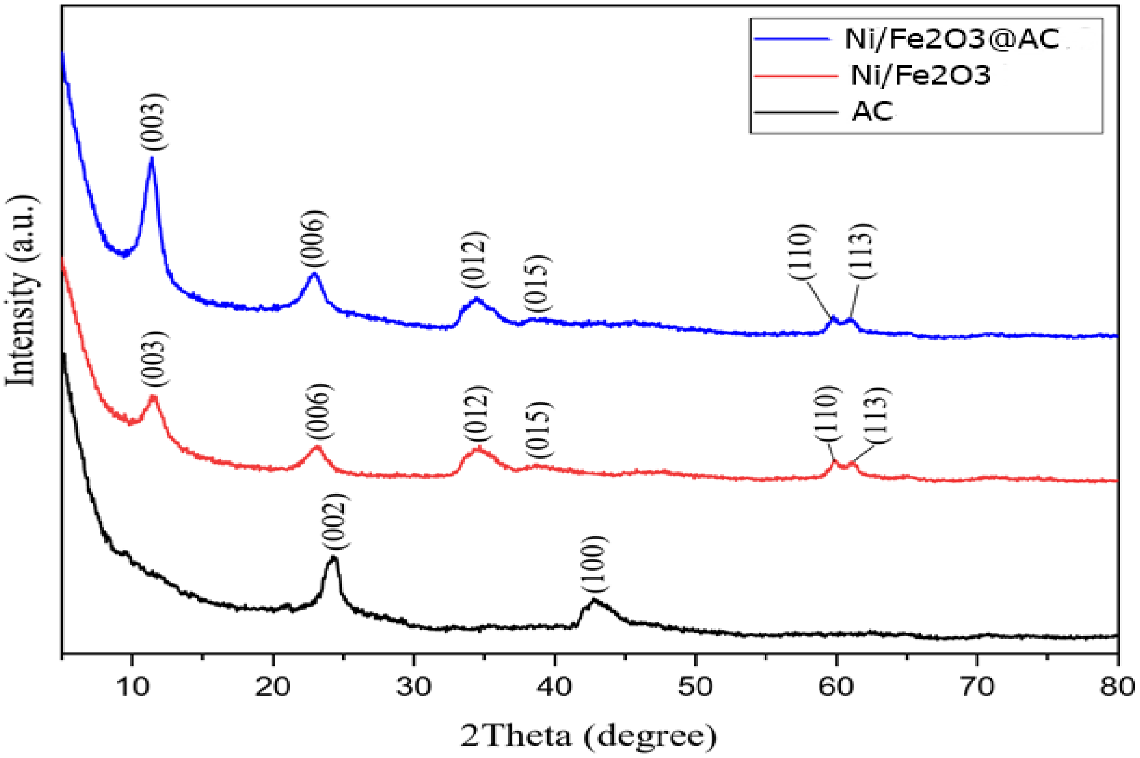

Figure 3: XRED Pattern of Ni/Fe_2O_4 AC

Table 3: Surface Area and Pore Characteristic of Different Samples of Activated Carbon Supported Ni/Fe_2O_3 Catalyst

Samples	BET Surface Area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
AC	1097.96	3.444	0.945
Ni/Fe_2O_3	103.173	4.553	0.117
Ni/Fe_2O_3 @AC	543.169	3.383	0.459

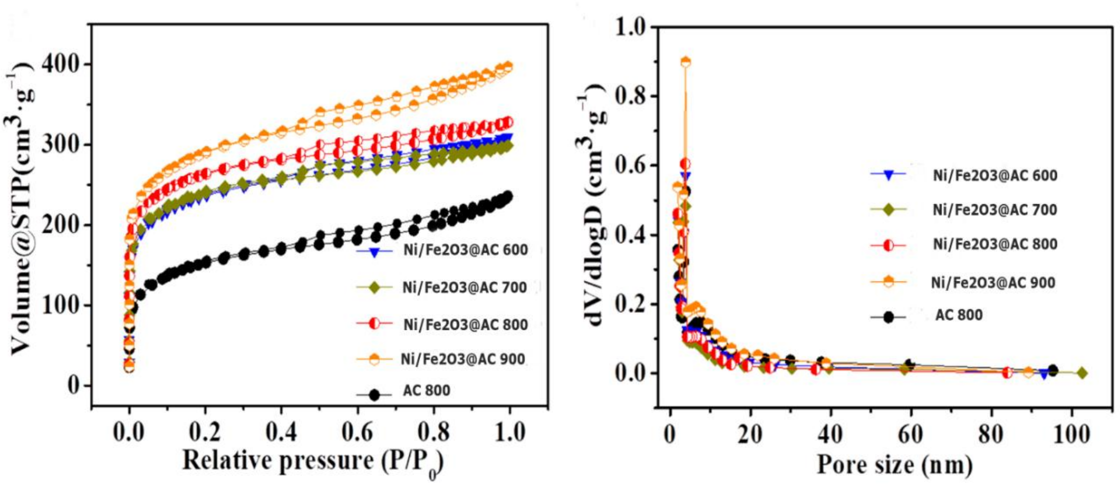

Figure 4:Activated Carbon Supported Ni/ Fe_2O_3 Catalyst (a) Adsorption isotherm (b) Pore Size distribution.

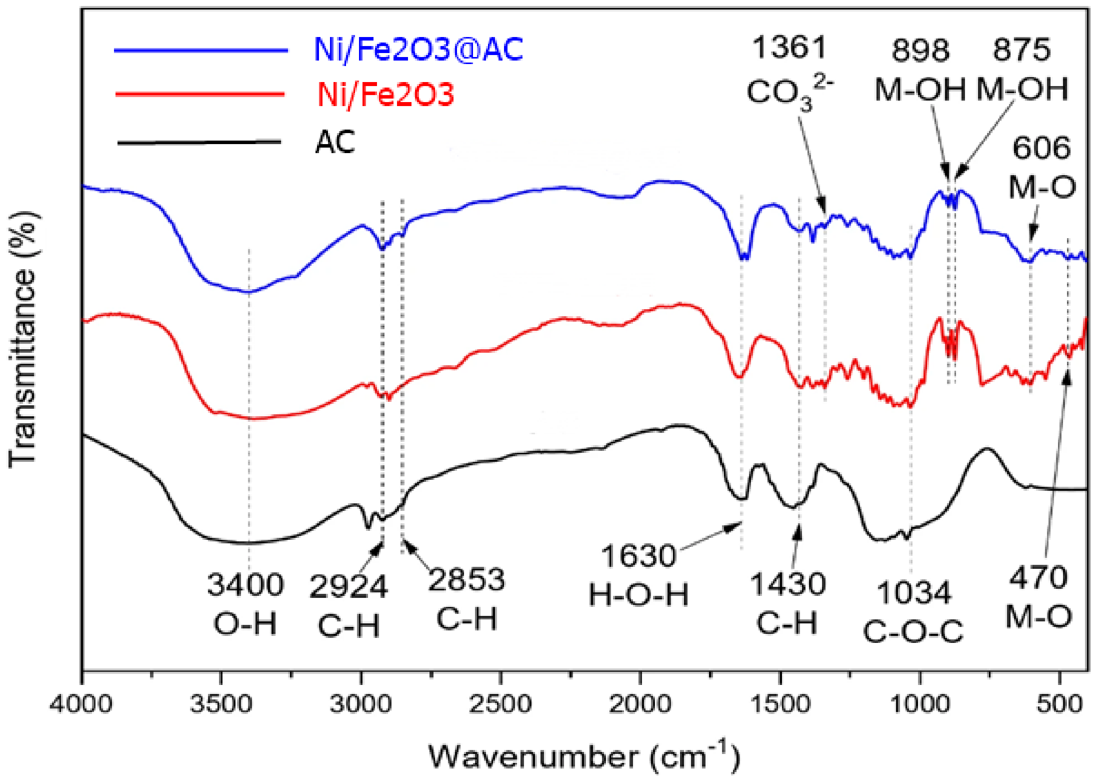

Figure 5: FTIR Activated Carbon Supported Ni/ Fe_2O_3Catalyst

Effect of Catalyst on HTL Performance

The incorporation of the $NiFe_2O_4$/activated biochar catalyst led to a marked improvement in bio-crude yield and quality relative to non-catalytic HTL. The catalyst facilitated deoxygenation and aromatization reactions, increasing the bio-crude HHV to

16.66 MJ kg^{-1} and carbon content to 63.53 wt%. These enhancements are consistent with previous studies reporting the effectiveness of bimetallic transition metal catalysts in promoting hydrogen transfer and C–O bond cleavage under hydrothermal conditions (Huang et al., 2021; Wang *et al.,* 2023). Table 4 shows catalyst increased bio-crude C-content (63.53 wt% vs. 57.26 wt%) and HHV (16.66 MJ/kg vs. 15.84 MJ/kg), with O-reduction (24.54 wt%). Figure 6 illustrates optimal yields at 320°C.

Table 4: Ultimate Analysis of Bio-crude from MFW Hydrothermal Liquefaction with and without Activated Carbon Supported Ni/ Fe_2O_3 Catalyst

Parameter	**Without Catalyst (wt.%)**	**With Catalyst (wt.%)**
Carbon (C)	57.26	63.53
Hydrogen (H)	7.23	7.68
Nitrogen (N)	3.35	4.23
Sulfur (S)	0.02	0.02
Oxygen (O)*	32.14	24.54
Higher Heating Value (MJ/kg)	15.84	16.66

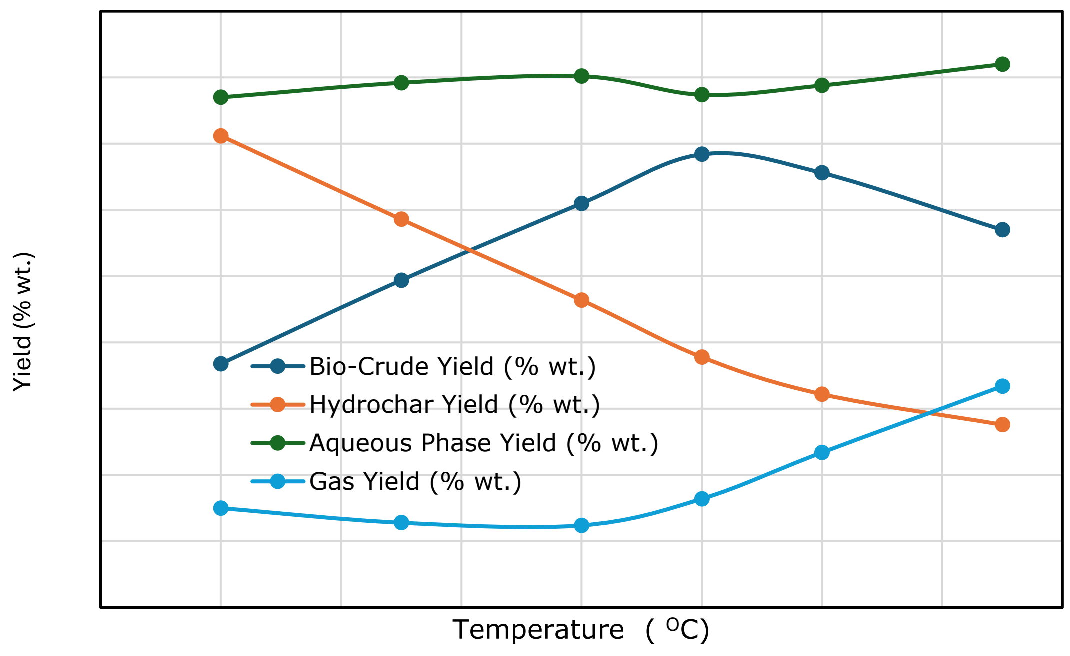

Figure 6:Effect of Temperature on Bio-Crude and Hydrocar Yields

Bio-Crude Composition and Comparison

GC–MS analysis showed that the bio-crude consisted predominantly of aromatic hydrocarbons, phenolic compounds, and nitrogen-containing heterocycles. The observed shift from oxygenated species toward more thermodynamically stable aromatic compounds indicates enhanced upgrading pathways facilitated by the bimetallic catalyst. Similar compositional trends have been reported for catalytic HTL systems employing nickel- and iron-based catalysts (Wang et al., 2023; Xu *et al.,* 2020). Figure 7 GC-MS reveals catalyst-driven shift to aromatics/phenolics (e.g., phenol 12.45%, tetradecane 7.11%). Table 5 compares with literature: current $NiFe_2O_4$/AC excels in deoxygenation/aromatization vs. HZSM-5, Ni/Al_2O_3, outperforming thermal HTL

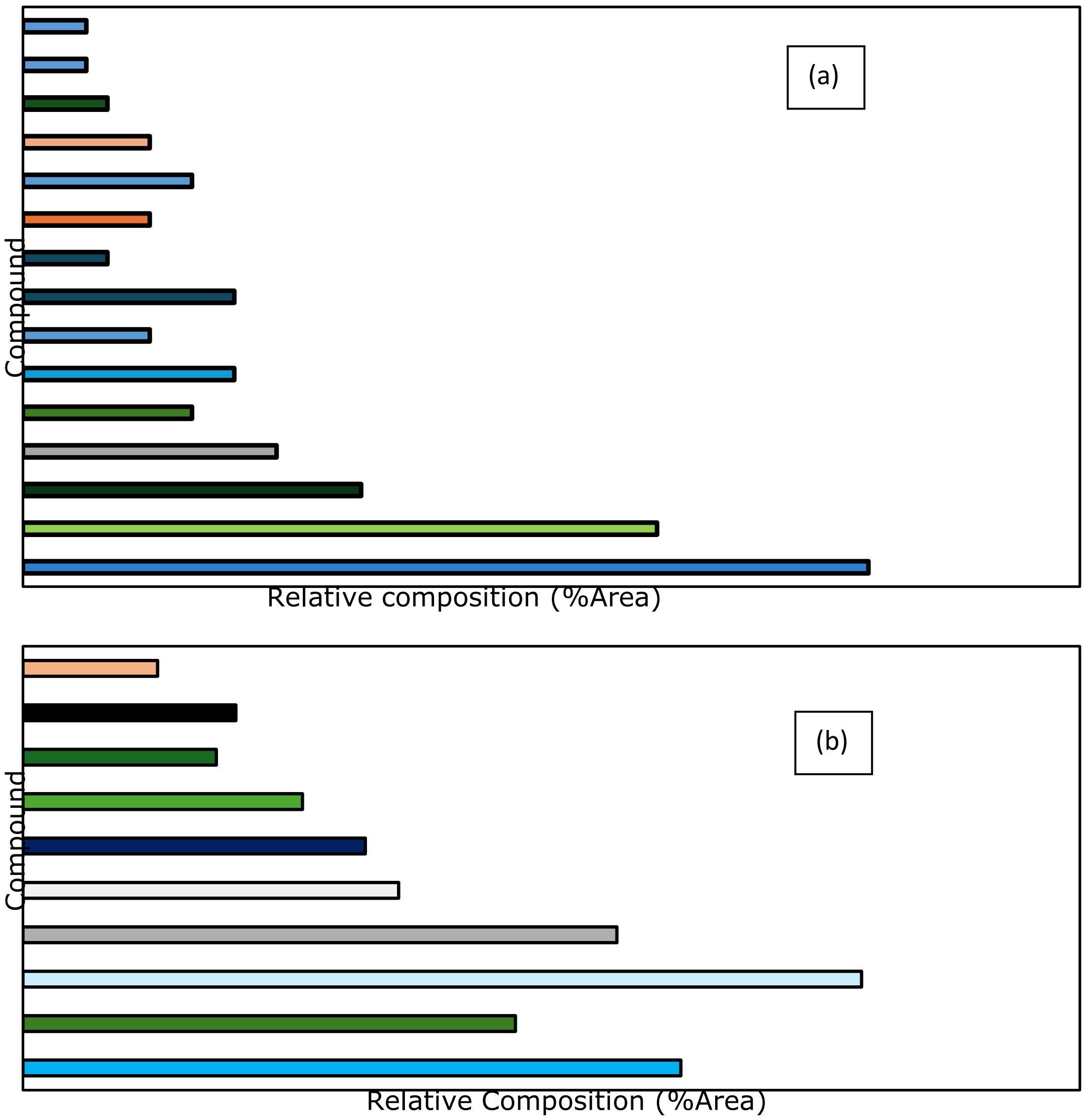

Figure 7: Biocrude Compounds from HTLof MFW (a) Thermally (b) Over Template-Synthesized Activated Bio-char Supported Bimetallic Catalyst

Table 5: Comparative Analysis on Bio-oil Upgrading Produced from HTL of MFW

	Thermal	**Current Catalyst (Biochar-Bimetallic)**	**HZSM-5**	**Ni/Al_2O_3**	**Co/MgO**
Major fatty acid	Palmitic acid (20%)	Palmitic acid (15.87%) + methyl ester (11.24%)	Reduced, esters formed via cracking	Reduced, FAMEs + alkanes	Reduced, increased C8–C18 esters
Aromatic content	Phenol (8%), Guaiacol (6%)	Phenol (12.45%), p-Cresol (9.32%)	High: Benzene, Toluene, Xylenes (BTX)	Moderate: Phenol, Cresols	High: Cresol, Phenol derivatives
Oxygenates (acidic/furanic)	Acetic (5%), Formic (2%), Furfural (3%)	Largely absent	Strongly reduced, <1%	Reduced, still some residual acids	Strongly suppressed
Hydrocarbons	Hexadecane (3%)	Tetradecane (7.11%), Nonadecene (6.48%)	High: Aromatic & aliphatic HC	Moderate alkanes and alkenes	Alkenes and long-chain paraffins
Nitrogenous compounds	Indole (2%)	Benzamide (3.66%)	Trace amounts	Slightly retained	Slight presence of N-heterocycles
Ketones	Cyclopentanone (5%)	Cyclopentanone (2.55%), Acetophenone (5.29%)	Moderate (e.g., Acetophenone)	Low yield of ketones	Acetophenone, cyclopentanone
References	—	Current Study	(Zhang et al., 2024)	(Elliott et al., 2023)	(Toor et al., 2022)

CONCLUSION

This study successfully demonstrated the conversion of mango fruit waste into upgraded bio-crude oil (HHV 16.66 MJ kg^{-1}, C 63.53 wt%) via catalytic hydrothermal liquefaction using template-synthesized $NiFe_2O_4$/activated biochar. The bimetallic catalyst significantly enhanced deoxygenation, aromatization, and hydrogen transfer, yielding superior fuel quality compared to non-catalytic processing and other reported systems. These findings establish mango waste as a viable feedstock and engineered biochar-supported catalysts as promising for scalable waste-to-energy conversion, advancing circular bioeconomy principles. Future research should explore catalyst recyclability and continuous-flow reactor integration.

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